(12) UK Patent Application (19) GB (11) 2 304 628 (13) A

(43) Date of A Publication 26.03.1997

(21) Application No 9518189.7

(22) Date of Filing 07.09.1995

(71) Applicant(s)
Kodak Limited

(Incorporated in the United Kingdom)

Patent Department, Headstone Drive, HARROW, Middlesex, HA1 4TY, United Kingdom

(72) Inventor(s)
Michael Ridgway
Colin James Gray

(74) Agent and/or Address for Service
R F A Nunney
Kodak Limited, Patent Department, Headstone Drive, HARROW, Middlesex, HA1 4TY, United Kingdom

(51) INT CL[6]
B41C 1/10 , B41M 1/06 , B41N 1/08 3/03

(52) UK CL (Edition O)
B6C CHB C621
U1S S2240 S3020 S3021

(56) Documents Cited
GB 1490732 A US 5145758 A US 4872962 A
US 3914125 A

(58) Field of Search
UK CL (Edition O) B6C CHB CSAB
INT CL[6] B41C 1/04 , B41M 1/06 , B41N 1/08 3/03
ONLINE DATABASES: WPI,CLAIMS,EDOC,WPIL

(54) Printing plate product

(57) A lithographic printing plate product comprises a support having a metallic surface layer characterised in that the metallic surface layer has a chemical compound adhered thereto via a group which will bind it to the metal surface, the compound also having either an oleophilic group which will render the surface hydrophobic or a group which will render the surface hydrophilic and wherein the compound can either be removed or altered by electrolysis to provide a compound which no longer renders the metal surface oleophilic or hydrophilic respectively.

GB 2 304 628 A

2304628

PRINTING PLATE PRODUCT

Field of the Invention

This invention relates to a printing plate product, and to a method of forming a lithographic printing plate in which the image is formed by an electrochemical reaction.

Background of the Invention

In the widely used lithographic printing process a printing plate is planographic, the background areas are hydrophilic and image areas are hydrophobic or oleophilic. In the printing machine rollers apply an aqueous solution and other rollers apply oily ink to the surface of the plate. The water on the hydrophilic areas of the plate prevents the ink adhering to those areas while the ink is deposited on the oleophilic areas. The term planographic does not imply that a printing plate is flat, as lithographic plates are usually carried on cylinders, but merely implies that the images are not carried by raised areas, as in the case with intaglio or gravure printing plates.

Many ways of making such printing plates have been described. Most of these require an imagewise light exposure of the desired image onto the plate itself or as a precursor thereof, eg a high contrast photographic negative or positive film. As is well known the reproduction of a continuous tone image is achieved by breaking the image up into a regular array of dots of different sizes.

Problem to be Solved by the Invention

The printing industry is constantly looking for new methods of forming printing plates which are simpler to produce, of higher quality and/or easier to use than is currently available. Methods of making printing plates have been devised in which an image is recorded on a plate by an electrochemical reaction

using electrodes, to avoid the need for the use of a light sensitive plate and a high contrast photographic film image. However the known processes are still quite complex and have a number of drawbacks. In particular, the known processes have high current and energy requirements because of which the plates can, in practice, only be written on a punctiform or point by point basis. As well as being inefficient in terms of energy usage, the plates also take a long time to write. There is thus a requirement for a simpler, more efficient, printing plate which requires less current to write an image onto that plate.

US-A-4718340 discloses a reusable printing plate comprising a hydrophilic plate material, such as nickel, coated with a hydrophobic layer. The hydrophobic layer is selectively removed by electric spark discharge, by a beam of electromagnetic energy, such as a laser beam, or a beam of ionised particles applied via a matrix of styli or electrodes. The disadvantage with this approach is that the apparatus has high energy requirements. In the preferred approach, which utilises spark discharge, an inert gas is required in the arc region to reduce the required breakdown voltage. Even so voltages of 300 to 1000 volts are still required to operate the apparatus. If an array of electrodes were used which would be difficult because of the electrical energy requirements for operating that array, mutual interference would occur between the electrodes, if the electrodes were too close together. This would result in a loss of definition in the resultant image on the printing plate.

US-A-4872962 discloses a printing image carrier coated with a hydrophobic polymer (polypyrrole) which can be oxidised electrochemically into a charged state

which is a hydrophilic monomer. Electrochemical reduction in an electrolyte such as ammonium bromide reverses the process. The problem with this process is that the compounds used are expensive. Also the process of converting a monomer to a polymer and vice versa is indeterminate due to the indeterminate nature of a polymer in terms of molecule size. As a result, the resolution of the process and the resultant printing plate are poor. Further the process has a high current requirement which means that in practice it is difficult to electrolyse the image onto the plate on much more than a point by point basis.

US-A-5145758 is a related patent to US-A-4872962 and discloses a similar process for making a printing plate in an offset litho type of printing press. In the described process a printing image substrate carrier such as nickel is washed, coated with a liquid monomer and a polymer is electrochemically produced at desired locations on the substrate by oxidising the liquid monomer. If the substrate is hydrophobic, the polymer is hydrophilic and vice versa. The process described is almost identical to that described in US-A-4872962 and suffers from the same problems.

GB-A-2262067 discloses a lithographic type planographic printing press which includes a printing plate or forme having hydrophobic and hydrophilic areas corresponding to an image to be printed. In the method of making the plate, the plate is first coated with a hydrophilic layer of fluid such as a plastic containing diazonium compounds or a diazoquinone. The layer is then selectively removed in an electrolyte, such as potassium chloride. The remaining hydrophobic areas not removed by the electrolysis correspond to the desired image. The current flow device effects the removal of the fluid areas by dissolving the fluid

in acids or alkali formed by the current flow. Consequently the fluid must be soluble in acid or alkali. Because the remaining image defining areas of the fluid are soluble in acid or alkali the plate must be further processed to preserve the image. Thus, the plate is then treated with a processing device which emits ultraviolet, light or heat radiation. One disadvantage of this process is that it involves a large number of stages. Being a fluid, the hydrophobic fluid has to be applied to the plate just prior to the electrochemical reaction. Further, the fluid has to be an energy reactive material sensitive to light or heat in much the same way as standard light sensitive lithographic plate. These characteristics of the fluid create storage problems and mean that the fluid has a limited useful life and that the plates cannot be prepared in advance of the selective removal of the fluid as their useful product life would be short. In the event that the fluid is a 'foil' which is a given alternative in GB-A-2262067, then the foil has to be quite thick to have sufficient mechanical strength. It would thus take a substantial amount of electrical energy to remove the non-image areas. As well as increasing the energy requirements this will also create problems of gumming up during the selective removal of the layer due to the quantities of removed fluid dissolved or mixed in the electrolyte. There is a danger that fluid which has been selectively removed from the plate will stick to the areas of the printing plate which were intended to be fluid free. This problem will also occur even if the fluid is a liquid. The plate itself includes a matrix of electrodes and consequently each plate is expensive. GB-A-2262067 suggests that the fluid which remains on the roller after the selective removal of

the non-image areas may be the ink for printing an image. Although this avoids the need for a radiation treatment stage, clearly only one print could be made following each selective fluid removal process.

US-A-4614570 discloses a printing plate formed from a multi layer material comprising an electrically conductive layer and a reproduction layer. Again polymers are the preferred material for the reproductive layer. The non-image areas of the reproduction layer are selectively dissolved by the action of electric current applied via a stylus shaped electrode. Dissolving is caused by increased pH value by discharge of H+ ions in the region of the electrodes. This system has the disadvantage that large quantities of hydrogen are evolved. This creates safety problems as hydrogen is explosive. Also the increase in pH value can corrode the support for the reproductive layer. Again this process requires substantial amounts of electrical energy to work. The use of polymers as the reproduction layer makes the resolution of the plate poor and dissolved polymers in the electrolyte will tend to gum up the process and may adhere to areas of the plate which are intended to be free of polymer.

Summary of the Invention

According to the present invention there is provided a lithographic printing plate product initially comprising a support having a metallic surface layer characterised in that the metallic surface layer has a chemical compound adhered thereto via a group which will bind it to the metal surface, the compound also having either an oleophilic group which will render the surface hydrophobic or a group which will render the surface hydrophilic and wherein the compound can either be removed or altered by

electrolysis to provide a compound which no longer renders the metal surface oleophilic or hydrophilic respectively.

Typically, the chemical compound is initially present as a monolayer, i.e. a layer which is one molecule in thickness, extending over the metallic surface.

Preferably, the metallic surface layer is composed of silver or copper.

The metal-attracting group may be a mercapto group (-SH).

Suitable chemical compounds having a hydrophobic (oleophilic) group include phenylmercaptotetrazole and 1-n-dodecanethiol.

2-mercaptoethane sulphonate is an example of a suitable hydrophilic chemical compound.

In one preferred embodiment the chemical compound is removed by oxidation by electrolysis using an electrode which is electrically negative with respect to the plate.

In another embodiment the compound is a mercaptan including an azo group and an oleophilic group, with the mercapto group and the oleophilic group disposed on opposite sides of the azo group and the azo group can be converted by a reduction in acid into a hydrophilic amine group by means of an electrode which is electrically positive with respect to the plate.

The invention also provides a method of forming a lithographic printing plate which comprises imagewise applying an electric current to a printing plate precursor comprising a support having a metallic surface as described above and oxidising the compound imagewise by electrolysing using an electrode which is electrically negative with respect to the plate to

provide a compound which no longer renders the metal surface oleophilic or hydrophilic respectively.

The present invention also encompasses a method of printing using a printing plate prepared from a printing plate product as described above, characterised by using a fountain solution which includes a hydrophilic group that will bind to the metallic surface where that surface is not oleophilic.

Advantageous Effect of the Invention

The present invention provides a lithographic plate material which can be used to form a lithographic printing plate without using an imagewise light exposure but which can be imaged using an image in electronic form. The imaging process relies on the breaking of a series of chemical bonds attaching a hydrophilic or oleophilic molecule to a plate. This requires much less energy than dissolving plastics in acid or alkali or converting polymers into monomers or vice versa. The accuracy or resolution of the recordal of an image on the printing plate product is also improved. The low energy requirements enable a plate to be written line by line rather than on a point by point basis. This enables a printing plate to be written in as little as a few seconds.

The layer can, and is preferably, a monolayer, that is a single layer of molecules bound to the plate. If the plate includes mercapto (SH-) groups bound to silver then the silver will bind to the sulphur molecule. It is believed that the silver displaces the hydrogen atom. The rest of the chemical compound will extend generally perpendicularly away from the plate and terminate in either a hydrophilic or an oleophilic group. By using a monolayer, the minimum quantity of chemical compounds are required for each plate. This is much cheaper than using

comparatively thick layers of polymer mechanically bound to the plate. Also during selective removal of the compound to form an image on the plate only very small quantities of removed material become dissolved or mixed into the electrolyte and these do not affect the process. Further it is believed that the binding mercapto group is destroyed by the oxidation process, and thus would no longer bind to the plate. The accuracy and resolution of an image recorded onto the printing plate product are also improved over the existing prior art plates discussed above. Also because very low currents are employed in writing images onto the printing plate product, negligible quantities of hydrogen are given off in the process of forming an image on the plate.

The plate is not light sensitive, can be prepared in advance and stored and can have a long shelf life.

Further, as is well known, during electrolysis, the electrode at which oxidation takes place (the anode), is degraded. In preferred embodiments of the present invention, the printing plate product is the anode Although, in theory, the printing plate product is reusable, the plate only requires electrolysing once which will not harm the plate significantly. Reduction, which is not generally harmful to electrodes, will take place at the writing electrodes which are usually more expensive and which it is more important to protect from degradation.

Detailed Description of the Invention

The metal which forms the metallic surface layer of the printing plate may be any of the metals in group 2 of the periodic table including, inter alia, bismuth, cadmium, arsenic, antimony, tin, zinc, manganese, cobalt, and nickel. However, copper and silver are the preferred metals for the plate. The

layer does not need to be very thick. For example, if the metal is silver, a layer of one micron thickness is sufficient.

The group which will bind the compound to the metal surface will depend on the metal. However the preferred group, particularly for silver and copper is a mercapto group (-SH). Using a mercapto containing compound it is a simple process to chemically bind the compound to the copper or silver surface. The compound may be painted or washed over the silver or copper plate in solution: the hydrogen atom in the mercapto group is displaced and the sulphur binds to the silver or copper.

The printing plate support may comprise any conducting plate the preferred material being a metal.

The metal surface layer may be applied to the plate by any suitable process, for example electrolysis.

Once the printing plate product has been prepared, and image is recorded onto the plate. In most of the embodiments of the present invention this is done by selectively removing the mercapto compound from the plate by oxidation using an electrode or, preferably, an array of electrodes. The electrode is normally negative with respect to the place, although this is not the case if the image is formed by reduction of an azo compound which is discussed at the end of this specific description.

There are two types of printing plate product - negative writing plates and direct or positive writing plates.

In negative writing plates the plate is coated with a hydrophobic/oleophilic layer. The areas where the layer is removed are then either intrinsically

hydrophilic or are made hydrophilic. In the present invention this may be done by washing the plate with a hydrophilic compound, such as a thiosulphate or a hydrophilic mercaptan, that will bind to the exposed areas of the metallic surface layer from which the oleophilic mercaptan has been removed.

In positive writing plates the plate product is coated with a hydrophilic layer and the areas which are removed are either intrinsically hydrophobic or are made hydrophobic. This can be done by washing the plate with a solution of a hydrophobic mercaptan.

Images recorded on lithographic printing plates are made up of a large number of tiny dots. In half tone images the size of the dots varies depending on the contrast required. If we consider an image to be made up from a grid of tiny squares each one potentially containing a dot, then the size of the dot in each square determines the density of the image. Writing a positive plate is intrinsically a more accurate process because the current applied generally directly determines the area of a dot, until the circumference of the dot approaches the perimeter of the square. Thus, it is much easier to control the size of the dots. For example if a particular dot was intended to occupy 20% of an area of a square then a 10% error in writing, caused by applying the desired current to the writing electrode for 10% too long would increase the size of the dot by only 10%, to 22%, which would not be a significant error. However, in a negative writing system, to create a dot occupying 20% of a square, 80% of the area of the square has to be removed: a 10% error either way would either leave one with a dot occupying 12% of the area of the square or 28%. Thus in negative writing errors can be much more significant. Thus positive writing

electrodes are generally preferred although as the following examples show the present invention can provide either positive or negative writing plates.

As is common with many lithographic plates, however made, there is a tendency for scumming (adherence of ink to hydrophilic areas) to occur after plates made according to the present invention have been used to make a substantial number prints in a lithographic printing press. Scumming can be inhibited by adding a chemical, chosen so that it binds to an unprotected metallic surface, and which makes the surface hydrophilic but which will not bind to the metallic surface which is protected by the hydrophobic mercaptan. Although, in theory, all of the metallic surface should be covered by either a hydrophobic or hydrophilic compound, unless the metallic surface is intrinsically hydrophobic or hydrophilic, it is possible that some hydrophilic compounds can become detached from the metallic surface during printing. Use of a suitable chemical in the fountain solution will alleviate this problem. Suitable chemicals if the metallic surface is silver include a dilute hydrophilic mercaptan or a thiosulphate such as is commonly used in photographic fixer.

The following examples are included for a better understanding of the invention.

EXAMPLE 1.

A positive writing plate product was made as follows. A smooth copper plate was cleaned with 1600 grade emery paper. Copper is intrinsically hydrophobic. The surface was cleaned with Kodak 3000 fixer diluted 1 part fixer to 3 parts water. The active ingredient of the fixer is thiosulphate which

will remove impurities such as copper sulphide on the plate.

The surface was washed with a solution of 0.3 gram 2-mercaptoethane sulphonate, a hydrophilic mercaptan, as a sodium salt, dissolved in 30cc water. The surface was then wiped and dried with a tissue.

The surface is now ready to have an image written onto it by selective oxidation of the mercaptan by electrolysis such as by an electrode as described in co-pending UK patent application No.....entitled 'Electrode for use in writing information on a printing plate', filed concurrently herewith in the name of Kodak Ltd, although any suitable electrode and electrolyte could be used to record an image on the plate. The oxidised areas, where the compound has been removed from the copper, are hydrophobic and define the desired image.

EXAMPLE 2.

Another positive printing plate product was made as follows. The same procedure as described above in Example 1 was carried out on a silver plate. However, because silver is not intrinsically hydrophobic, after electrolysis had been carried out it was necessary to make the silver surface hydrophobic in the image areas where the 2-mercaptoethane sulphonate had been removed. The surface was washed with dodecanethiol, a hydrophobic mercaptan, and allowed to stand for two minutes. The dodecanethiol bound to the exposed areas of silver. The surface was then polished to remove excess dodecanethiol and washed with ethanol. The surface was then ready for printing.

EXAMPLE 3.

A negative printing plate product was made as follows. A silver plate was prepared by cleaning it with 1600 grade emery paper. The plate was then

painted with a solution of 0.5 gram phenylmercaptotetrazole in 30cc of a one to one mixture of ethanol and water. Phenylmercaptotetrazole is a hydrophobic mercaptan. The plate was then polished with a dry tissue to remove excess phenylmercaptotetrazole. Next, the plate was painted with dodecanethiol left to stand for 5 minutes and polished with a dry tissue. Dodecanethiol is also a hydrophobic mercaptan. Although in theory it would only be necessary to coat the silver in either phenylmercaptotetrazole or dodecanethiol to make the plate hydrophobic, it has been found that using both compounds improves the printing plate. The surface was then cleaned with a tissue soaked in ethanol.

The plate was then tested to see if it was hydrophobic by brushing it with a water based ink. The ink did not adhere to the plate.

The plate was tested as follows. A small drop of a molar solution of sodium chloride was placed on the surface. The drop of salt solution was connected to a tinned copper cathode, with the plate acting as an anode and a voltage of 5 volts was applied. The plate was then dried with a tissue. The plate was then wiped with a tissue dampened with Kodak 3000 fixer diluted 1+3 with water and then wiped with a damp tissue to remove excess fixer. The thiosulphate in the fixer is hydrophilic and binds to the silver to make the plate hydrophilic in those areas.

A water based ink was then brushed onto the plate. The water based ink adhered to the hydrophilic areas, where electrolysis had taken place, but not to the oleophilic areas. This demonstrates the principal of the invention.

EXAMPLE 4.

A negative printing plate product was prepared as described above in Example 3 up to the stage where the plate was cleaned with ethanol, ie before the plate was tested with ink or electrolysed.

An image was then written on the plate as follows.

A pen with a fibre tip and a water soluble ink was cut open at the top end and the ink was washed out by prolonged stirring in water with frequent changes of water. The pen was then dried. A wire was then wrapped around the fibre tip of the pen in such a way that the wire did not project below the writing tip of the pen. The pen was then filled with a molar solution of sodium carbonate which acted as an electrolyte.

The pen was then connected to a conventional plotter controlled by a computer in place of the standard plotter pen. The wire attached to the tip of the pen was connected to a 5 volt DC power supply.

An image was then written on the plate by the computer driven plotter in the normal way. Where the pen passed over the plate the mercaptan was oxidised and removed from the plate. It was possible to move the computer controlled printer at the maximum speed it would have been used to write on paper with ink and still form a satisfactory image.

The plate was then washed overall with a tissue wet with standard ammonium thiosulphate Kodak 3000 fixer diluted 1+3 with water. This rendered the exposed areas of the plate, from which the mercaptan had been removed, hydrophilic. The plate was then wiped and dried. The plate was then put on a printing press.

The fountain solution in the press was then replaced with Kodak 3000 fixer diluted 1 + 25 with

water. Fixer was used because it contains thiosulphate, which binds to silver and makes it hydrophilic. The press was then run in the normal way after wiping the plate with a fountain solution. Over 2000 copies were obtained when the press was stopped.

The printing plate product of the present invention can also be used in a stochastic printing process. In this process the dots are all of an identical size which is generally much smaller than the average size of a dot on a half tone plate. Normally, because the dots are small, the resolution requirements for this process are too high for existing electrode based writing systems. However because the printing plate products of the present invention produces a resolution of molecular accuracy, stochastic plates are possible.

As an alternative to the oxidation of a mercaptan as is described above, it would be possible to use an oleophilic mercapto compound including an azo N=N group. In this case the mercapto group would again bind to the metallic surface layer of the plate. The azo group would be present in a chain linking the metal-sulphur bond (where the mercapto group binds to the metallic surface layer) to the oleophilic group. In this case an acid reduction of the azo link group by an electrode would break the chain at the N=N link leaving a hydrophilic amine (H-N-H) group. This type of plate would be a negative writing plate.

CLAIMS:

1. A lithographic printing plate product initially comprising a support having a metallic surface layer characterised in that the metallic surface layer has a chemical compound adhered thereto via a group which will bind it to the metal surface, the compound also having either an oleophilic group which will render the surface hydrophobic or a group which will render the surface hydrophilic and wherein the compound can either be removed or altered by electrolysis to provide a compound which no longer renders the metal surface oleophilic or hydrophilic respectively.

2. A lithographic printing plate product according to in claim 1, characterised in that the chemical compound is initially present as a monolayer extending over the metallic surface.

3. A lithographic printing plate product according to claim 1 or claim 2, characterised in that the metallic surface layer is composed of silver or copper.

4. A lithographic printing plate product according to any of claims 1 to 3, characterised in that the metal-attracting group is a mercapto group (-SH).

5. A lithographic printing plate product according to any of claims 1 to 4, characterised in that the chemical compound is phenylmercaptotetrazole or 1-n-dodecanethiol.

6. A lithographic printing plate product according to any of claims 1 to 4, characterised in that the chemical compound is 2-mercaptoethane sulphonate.

7. A lithographic printing plate product according to any of claims 1 to 6, characterised in

that the chemical compound is removed by oxidation by electrolysis using an electrode which is electrically negative with respect to the plate.

8. A lithographic printing plate according to any of claims 1 to 5, characterised in that the compound is a mercaptan including an azo group and an oleophilic group, with the mercapto group and the oleophilic group disposed on opposite sides of the azo group and wherein the azo group can be converted by a reduction in acid into a hydrophilic amine group by means of an electrode which is electrically positive with respect to the plate.

9. A method of forming a lithographic printing plate which comprises imagewise applying an electric current to a printing plate precursor comprising a support having a metallic surface as claimed in any of claims 1 to 7 and oxidising the compound imagewise by electrolysing using an electrode which is electrically negative with respect to the plate to provide a compound which no longer renders the metal surface oleophilic or hydrophilic respectively.

10. A method as claimed in claim 9, in which the compound initially renders the metal surface hydrophilic.

11. A method of printing using a printing plate prepared from a printing plate product according to any of claims 1 to 8, characterised by using a fountain solution which includes a hydrophilic group that will bind to the metallic surface where that surface is not oleophilic.

The Patent Office

18

Application No: GB 9518189.7
Claims searched: 1-11

Examiner: A.J.Rudge
Date of search: 20 November 1996

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): B6C(CHB,CSAB)

Int Cl (Ed.6): B41C-1/10;B41M-1/06;5/26;B41N-1/08;3/03

Other: ONLINE: WPI,CLAIMS,EDOC,WPIL .

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
X	US 5145758	(Man Roland) - eg col.3,lines 41 et seq	1-2 at least
X	US 4872962	(MAN) - eg col.2, lines 40 et seq, & claim 1	"
X	US 3914125	(3M) - eg col. 3, lines 9 et seq	"
A	GB 1490732		

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.